THE

SCIENTIFIC PROCEEDINGS

OF THE

ROYAL DUBLIN SOCIETY

VOL. 25 (N.S.).

No. 7. JULY, 1949.

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DUBLIN :
PUBLISHED BY THE ROYAL DUBLIN SOCIETY.
BALLSBRIDGE, DUBLIN.
HODGES, FIGGIS, AND CO.,
6 DAWSON STREET, DUBLIN.
WILLIAMS AND NORGATE,
36 GREAT RUSSELL STREET, LONDON, W.C.1.
1949.

Price : One Shilling and Sixpence

IRISH MYCOLOGICAL INSTITUTE
31 AUG. 1949

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THE COMPOSITION OF IRISH DRINKING WATERS, WITH SPECIAL REFERENCE TO THE DISTRIBUTION AND SIGNIFICANCE OF FLUORIDE.

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[Read December 14, 1948. Published July 28, 1949.]

Significance of Fluoride.

Fluorine acquired a pathological significance early in the present century when feeding experiments showed that it accumulated in bones and teeth, producing structural changes and defects, the most familiar of which is the mottling of the dental enamel.

Mottled enamel, a developmental defect of the teeth, was first noticed amongst emigrants from Pozzuli, Italy, in 1901 by Eager, of the U.S. Public Health Service, and has since been observed to occur endemically throughout the world, notably in U.S.A., China, Africa, India, Spain, Italy, Holland, S. America, and in several small localised areas of England.

From the time of the first recorded investigations, suspicion was cast on the water supply. Some abnormal constituent was believed to be the cause, but its exact nature was not discovered until 1931, when Churchill reported the presence of fluoride in the waters of endemic areas of the United States, and Smith, Lantz, and Smith (1931) reproduced fluorosis in experimental animals fed on diets containing either (*a*) sodium fluoride or (*b*) the residue of drinking water from the affected town. Ample evidence has since been forthcoming to confirm the responsibility of fluoride in drinking water for this condition in man, and similar effects have been shown in the teeth of domestic animals (Thresh, 1943). In Africa, where the condition is known as ' Darmous,' fluorine in the soil has been shown to cause bone disease in horses and cattle, in addition to the dental defect, and both these conditions, together with signs of acute poisoning, have been exhibited by workers in aluminium factories where fluorine is present in the dust (Roholm 1932). Such severe effects are, however, exceptional, and most cases of chronic fluorosis are limited to the teeth, and are due to the continued ingestion during early childhood of fluorides in the drinking water.

In mottled enamel, the damage is almost entirely confined to the permanent teeth, and occurs solely during the period of calcification, hence, it is children up to the age of 14 years who are specially susceptible. The defect does not become

manifest until the teeth have erupted. As little as one part per million of fluoride in the drinking water is sufficient to cause mottling of the teeth (Greenwood, 1940). The number of people exposed to a fluoride hazard is unknown; but it is estimated that in the states of Texas and Illinois, U.S.A., alone, about 900,000 people are affected by fluoride in the water supply.

In 1936, Fink and Lindsay wrote: " With the rapidly increasing number of communities reporting fluorine-bearing waters, the occurence of fluorine toxicosis has taken an added significance and is now generally recognised as a serious public health problem."

The interest that was aroused in dental fluorosis resulted in a large number of investigations, and the fact gradually emerged that the incidence of caries amongst people living in areas where the water contains 1 ppm. or more of fluoride was very low, and that people with severely mottled teeth were practically immune from it. Dean (1938) and his colleagues showed that a lower incidence of caries was associated with a higher fluorine content, irrespective of whether the mottling was present or absent. Wilson (1941) gives a statistical review of the incidence of caries in high and low fluoride areas of England, with the same conclusion. Okerse (1944) states that the incidence of caries is related, not only to the fluoride content, but also to the pH and the hardness of the water, and where all three are high the incidence of caries is particularly low.

As a consequence of these results it was suggested (Ast, 1943) that a large scale experiment should be carried out to investigate the " caries-fluoride hypothesis " involving two towns of similar population and water supply, and that fluoride should be added to the water of one, the other being used as a control. Since it is believed that fluoride must be ingested during the years of tooth development the experiment would have to be continued until children who have no permanent teeth reach the age of 14, before the results can be assessed. This was opposed on the grounds that our knowledge regarding the continued ingestion of fluoride in small amounts over a period of years, under normal and pathological conditions, is incomplete (Gruebbel, 1944. Wolman, 1943).

The New York State Department of Public Health (1945) has begun an investigation of the " caries-fluoride hypothesis," using the two towns of Kingston and Newburgh, N.Y. Fluoride is being added to the water of Newburgh to the extent of 1.2 ppm.; that of Kingston contains no fluoride, and this town is taken as a control. The amount, 1.2 ppm., seems rather high, as 1 ppm. is said to be sufficient to cause mottling of the teeth.

The mode of action of the fluoride in producing this inhibition is unknown, though several theories have been put forward. The concentration at which it is effective suggests a catalytic effect or an inhibitory action on an enzyme system. Irrespective of the mode of action, however, the biological potency of fluoride is sufficient to demand a survey of its distribution, and of its availability in the natural surroundings of human communities, with special reference to water supplies, since they can contribute fluoride directly and indirectly in many ways to the diet.

Surveys have already been undertaken for the river and other water supplies of the U.S.S.R., several states in the U.S.A., areas of S. America, S. Africa, and in Great Britain. This is the first reported survey of the fluoride content of Irish drinking waters.

Origin of Fluoride-containing Water.

Two approaches to the problem suggested themselves.

(*a*) To test for the presence of fluoride in any conveniently obtained water, particularly from the centres of population throughout the country. The results of these random samplings are given below.

(*b*) To find out if there were any areas in Ireland where fluoride-containing waters were likely to be found.

In this country, as in England, almost all underground water supplies from wells and borings are derived from sedimentary rocks. Thus one might expect that any conclusions made as to the origin of fluoride-bearing waters in England would apply equally here. Wilson was assisted in her investigations of fluorosis in England by Bromhead (1941) of the Geological Survey. The reader is referred to the original papers for full details, but the conclusions may be summarised as follows.

Abundance of fluorspar does not make for water with a high fluoride content, fluorspar, CaF_2, being of very low solubility. In Derbyshire, one of the best known sources of fluorspar, Sutton (1936) has reported 43 waters, only one of which has a fluoride content of more than 1 ppm. The fluorosis of the Weardale fluorspar area is almost certainly a question of the source of the water supply, which is largely drawn from abandoned and flooded mines, in which the spar occurs. Where the more soluble fluorapatite is present fluorosis is likely to occur, as in the china clay district of St. Austel, Cornwall. It is possible that apatite may give rise to fluorosis, particularly when in contact with water of a high saline content. Almost 50 years ago, Carnot (1893) showed that fossil bones, consisting mainly of calcium phosphate, tend to take up fluorine, steadily approaching the composition of apatite with increasing age, and Bromhead suggests that " well water which is either derived from or is in contact with any phosphatic beds or with certain clays of marine origin " giving as examples the Jurassic clays and the Kimmeridge, Oxford, and Lias clays in descending order of stratification " is a possible source of fluorosis." Wilson has confirmed the presence of fluorosis in such districts.

Possible Occurence of Fluoride-containing Waters in Ireland

A preliminary survey was made to locate areas in Ireland, which might be sources of fluoride-containing waters.

The areas selected were:

(1) *The Namurian Shales of North Co. Dublin*

(2) *The Lough Neagh Clay*

(3) *North Clare*: the phosphate area near Doolin and the smaller area near Foynes, County Limerick (4) which is a continuation of the basal millstone grit shales (Fluorspar occurs in veins across Galway and Clare, and there is a vein near Doolin that was at one time prospected).

(5) *County Galway*: the metamorphic rock regions of West Galway, in which apatite occurs. There is little or no information as to the amount of apatite present, but the possibility of fluoride-containing waters occurring exists.
(6, 7 & 8) These three areas, *Kilkenny-Tipperary* (8), *Arigna* (7) and the area near *Kiltamaugh* (6) are all on the same level of the Yoredale Shales. In each of these regions phosphate has been reported to occur at the outcrop of the shale.

(9) Phosphate has also been reported on the Ordovician, near Courtown. It is probably present in very small quantity, but there exists the possibility that it might give rise to fluoride in the water supply.

The results of the analyses of waters obtained from these and other areas are given in the tables.

Methods of Analysis.

There is no universally accepted method for the estimation of fluoride in water supplies. Different methods have been adopted and modified, and in some cases at least it is difficult to assess the comparative values of the results. Several methods were investigated, preference finally being given to a zirconium-lake method, which, when modified, was found to be capable of detecting fluoride down to a concentration of 0.1 ppm.

The zirconium alizarin lake (which with the analogous hafnium compound is the only alizarin lake stable in acid solution) has been used for the estimation of fluoride by Casares and Casares (1930), Thompson and Taylor (1933), and J. M. Sanchis (1934). The method used by the author is based on that of Sanchis as modified by Lamarr (1945), and differs in the use of the sulphate instead of the nitrate of zirconium. The sulphate is much more satisfactory, being quite stable and non-deliquescent. The lake is stable and does not precipitate from the acid solution as the nitrate lake tends to do. Zirconium in the sulphate is anionic and in the nitrate cationic. Sulphate, chloride, phosphate, carbonate, and bicarbonate ions interfere with the estimation when present above a certain concentration. The carbonate and bicarbonate are removed by neutralization with nitric acid; the nitrate ion does not interfere. Potable waters rarely contain sulphate, phosphate or chloride in excess of these concentration limits.

The indicator is prepared in the following manner. Zirconium sulphate (0.25g.) is dissolved in a hundred millilitres of water. To this is added slowly and with constant stirring 25 ml. of sodium alizarin sulphate prepared by dissolving 0.37 g. of alizarin-S in 250 ml. of water. The red zirconium alizarin lake thus formed is made up to 500 ml. with distilled water, and 500 ml. of 2.1N sulphuric acid added. The solution is well shaken and allowed to stand for 4 hrs., during which time the colour changes from red to lemon yellow. It is then ready for use.

The following anions interfere when present above the concentrations stated:— Sulphate, 400 ppm.; chloride, 1000 ppm.; phosphate, 4 ppm.; carbonate, 100 ppm. (as $CaCO_3$) and bicarbonate, 122 ppm.

When the alkalinity exceeds the above values, it is neutralised with 0.164N nitric acid (1 ml. = 10 mg. HCO_3).

The procedure adopted for the analysis of the waters was as follows: (1) Determination of the total solid content. (2) pH determination. (3) Estimation of the chloride content. (4) Estimation of the sulphate content. (5) Estimation of the alkalinity. (6) Bleaching (if necessary). (7) Fluoride estimation. The sulphate figures are to be regarded as approximate and values below 15 ppm. are not given. The estimation was carried out by observing the depth at which a platinum wire was no longer visible in a cylinder of water to which bariuim chloride and hydrochloric acid had been added.

Many Irish waters are coloured, and it is necessary to remove this colour to carry out the colorimetric estimation. The waters were bleached with chlorine generated by dropping pure conc. HCl on to pure potassium permangate. Little chlorine is required, and if the chlorinated water is allowed to stand in a dark cupboard for some hours, the water is bleached clear. It is necessary to neutralise before bleaching, and to remove all chlorine, otherwise the zirconium lake will be decolorised. Complete removal may be tested for with *o*-toluidine.

The fluoride estimation is carried out on 100ml., bleached and neutralised if necessary. A series of standards are made up by adding from 1 to 20 ml. of the standard fluoride solution (1 ml. = 0.01 mg. F.) to a set of cylinders and making up to 100 ml. Ten ml. of the zirconium-alizarin indicator are added to each cylinder, and allowed to stand overnight. If fluoride is present the pink of the indicator will be bleached to any intermediate shade between pink and lemon yellow. The indicator is capable of detecting 0.1 ppm. of fluoride in a 100 ml. sample but for the detection of this amount the dimensions of the comparator tubes should be such that the height of the liquid in the tubes is approximately 20 cm.

Standard solution of fluoride.

Solution A. 0.2210 g.pure sodium fluoride in 1 litre 1 ml. = 0.1 mg.F.

Solution B. (1 ml. = 0.01 mg.F) is obtained by diluting *A* one tenth.

Waters giving a positive fluoride reaction were tested for phosphate. In no case was the concentration of phosphate found to exceed the limit given above.

Summary and Conclusions.

(1) A survey has been made of the fluoride content of Irish drinking waters from 42 different sources, including the principal sources of population.

(2) In only ten of the waters examined was fluoride found to be present, and then in concentrations of the order 0.2 ppm.

(3) These results suggest that the inhabitants of Ireland are not exposed to a fluoride hazard arising from the national water supplies. This conclusion is supported by collected medical and dental evidence of the rarity of fluorosis in the population.

(4) The therapeutic addition of fluoride to the Irish drinking waters, with a view to reducing the incidence of dental caries, though desirable, cannot be advocated until the results of the long term experiments now in progress in the United States of America have shown the wisdom of such a procedure.

The investigation was undertaken at the suggestion and under the supervision of Dr. W. R. Fearon, in the Department of Biochemistry, Trinity College, Dublin, and was made possible by a grant in aid from the Medical Research Council of Ireland.

I would like also to express my appreciation of the help and advice so willingly given by Prof. L. B. Smyth of Trinity College, and by Mr. Duffy and Mr. McCluskey of the Geological Survey of Ireland.

Distribution of Fluoride.

The analysis of a sample from any of the selected areas is prefixed by a number indicating the area.

The origin of the water supply is given in brackets.

A. Waters Containing 0.1 to 0.3 Parts per Million of Fluoride.

Solutes in parts per million.

Source	Total Solid (100°C)	F′	Cl	SO_4	Alkalinity (as ppm. $CaCO_3$)	pH	Date of Analysis
Co. Cavan.							
Virginia (Quilka res.)	124	0.2	12	∠15	30	7.2	April 1948
Co. Clare.							
(3) Ennistymon (Spring)	310	0.2	30	∠15	137	6.6	Aug. 1948
(3) Doolin (Well)	169	0.2	37	∠15	25	6.6	Aug. 1948
Co. Galway.							
(5) Galway (L. Corrib)	147	0.1	18	∠15	97	7.6	May 1948.
(5) Oughterard (Owenriff R.)	100	0.3	16	∠15	16	6.8	Oct. 1948
(5) Errisbeg West (Spring)	1132	0.2	245	39	247	7.6	Oct. 1948
Co. Limerick.							
Limerick (R. Shannon)	235	0.2	13	25	148	7.6	May 1948
Co. Monaghan							
Castleblayney (Res. nr. Carraig)	108	0.2	10	19	0	6.6	May 1948
Co. Tipperary.							
Tipperary (Galtee Mts.)	65	0.2	8	∠15		7.0	Dec. 1948
Co. Westmeath.							
Athlone (R. Shannon)	215	0.2	12	∠15	137	7.8	May 1948

B. Waters Containing Less Than 0.1 Parts Per Million of Fluoride.

Source	Total Solid (100°C)	F′	Cl	SO_4	Alkalinity (as ppm. $CaCO_3$)	pH	Date of Analysis
Co. Antrim.							
Belfast (Silent Valley res.)	102		12	∠15	56	7.6	May 1948
Co. Armagh.							
(2) Birches (Well)	540		51		260	7.8	Sept. 1948
Co. Carlow.							
Carlow (Kilesshan res.)	183		12	15	31	7.0	March 1948
Co. Cork.							
Cork	129		16	19	46	7.3	June 1948
Co. Dublin.							
Dublin (Vartry)	70		11	∠15		6.8	Jan. 1948
Dublin (Bohernabreena)	89		10	∠15		7.2	Jan. 1948
Dublin (Poulaphouca)	105		8			7.4	Jan. 1948
(1) Skerries (Naul res.)	247		19	37		6.8	June 1948
(1) Man O'War (Spring)	610		126	103		6.2	June 1948
(1) Ballaugh (Spring)	674		46	28	326	7.6	June 1948
(1) Lusk (Spring)	432		36	28	270	7.3	June 1948
Howth (St. Fintans Well)	465		38	∠15	139	7.0	March 1948
Co. Galway.							
(5) Roundstone (Spring)	150		33	∠15	21	7.0	Oct. 1948
Ballinasloe (R. Suck)	306		13	33	153	7.2	Oct. 1948
Co. Kildare.							
Naas (Well)	429		15	15	345	7.2	March 1948
Co. Kilkenny.							
Kilkenny (Douglas R.)	109		11	∠15	55	7.4	March 1948
Co. Meath.							
Rathmoylan (Well)	578		39	∠15	244	7.6	April 1948
Co. Monoghan.							
Carrickmacross (Coravoo res.)	288		14	21	188	7.6	May 1948
Co. Roscommon.							
Roscommon (Spring at Rockfield)	412		12	20	310	7.4	Oct. 1948
(7) Strokestown (Strokestown R.)	324		11	∠15	249	7.6	Oct. 1948
Co. Tipperary.							
Carrick-on-Suir (Comeragh Mts.)	59		8	∠15		6.8	Dec. 1948
(8) Kilsheelan (Slieve-na-Mon sth.)	44		11	∠15		7.0	Dec. 1948
(8) Mullinahone (Slieve-na-Mon nth.)	35		10	∠15		7.0	Dec. 1948

Source	Total Solid (100°C)	F'	Cl	SO_4	Alkalinity (as ppm. $CaCO_3$)	pH	Date of Analysis
Co. Westmeath.							
Kinnegad (R. Kinnegad)	464		11	15	324	7.0	Sept. 1948
Kilbeggan (Trib. of R. Brosna)	405		11	<15	270	7.8	Sept. 1948
Rathowen (Spring)	670		51	27	30	7.0	Sept. 1948
Mullingar (L. Owel)	189		12	<15	139	7.0	May 1948
Co. Wexford.							
Wexford (R. Sow)	173		19	33		7.0	May 1948
Gorey (R. Bann)	128		11	<15	19	7.2	May 1948
Enniscorthy (R. Slaney)	329		23	<15		7.0	May 1948
Co. Wicklow.							
Glen O' The Downs (Well)	412		20	<15	243	7.6	Nov. 1948
Arklow (Ballyduff res.)	154		16	<15		6.8	May 1948

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